SRI International

FINAL REPORT • February 24, 2004

PHOTOREDUCTIVE SEQUESTRATION OF CO$_2$ TO FORM C$_1$ PRODUCTS AND FUEL

For the period March 2002 to September 2003
SRI Project P11887

Prepared by:

Theodore Mill and Haruthai Tungudomwongsa

Award No. DE-FC-02NT41224

Prepared for:

U.S. Department of Energy
National Energy Technology Laboratory
Morgantown Site
P.O. Box 889
3610 Collins Ferry Road
Morgantown, WVA 26507-0880

Attn: Barbara Carney

DISCLAIMER

This combined report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agent thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

We have investigated the photochemical reduction of CO_2 in aqueous solution to form C_1 products using a variety of oxide semiconductors and near UV light. Conventional oxide photosemiconductors including TiO_2 and $SrTiO_3$, as well as modified oxide semiconductors including Pt/TiO_2 and $SrTiO_3/Cr$ – Sb, TiO_2/Fe_3O_4 or $TiO_2/Fe(CN)_6^{3-}$ were used. Analysis for formate, acetate, formaldehyde, methanol and methane were conducted by a variety of analytical methods. Despite extensive published data on the facile reduction of CO_2 by these semiconductors, we found only trace quantities of formate and acetate (typically less than 1 ppm) and no unequivocal evidence for formation of the other products.

The quantum efficiencies of TiO_2 and $SrTiO_3$ for forming formate and acetate from CO_2 are estimated to be 0.1-0.2% or less. The spectral properties of the unmodified oxides (TiO_2, $SrTiO3$) restricts their use of solar irradiation to about 10% of the available near UV and visible spectrum, thereby giving an overall quantum and spectral efficiency of less than 0.01%. Semiconductor oxides modified with, Cr and Sb, Fe_3O_4 or $Fe(CN)_6^{3-}$ exhibited no enhanced efficiency. However, Pt/TiO_2 does produce more formate and acetate than TiO_2 alone by about a factor of two.

Addition of 0.6 mM 2-propanol to an irradiated CO_2/TiO_2 suspension led to formation of larger amounts (0.55 mM, 25 ppm) of formate, but no formaldehyde. The higher yield is probably because re-oxidation of formate by semiconductor holes was competitively blocked by propanol acting as a sacrificial electron donor. Reoxidation of formate by TiO_2 under argon is 80 times faster than reduction. Thus, reoxidation could be an important process limiting the accumulation of products and will require new design strategies for reducing accumulation of products in the photocatalytic zone if the an efficient process is to be developed. New photosemiconductors are needed which have broad spectral absorbance extending to 600 nm.

Preliminary estimates were made of the physical size of a solar CO_2 photoreduction unit large enough to reduce the CO_2 produced from a 1000 MW coal-fired electricity plant. Although a perfectly efficient (100%) system could be as small as 10 km^2, to begin to approach that size plant footprint will require a dramatic improvement in semiconductor photocatalysis efficiency over that which is currently available.

CONTENTS

INTRODUCTION

The combustion-based production of CO_2 has evolved into what is perhaps the major environmental challenge of the 21^{St} century. Whereas, CO_2 levels in the atmosphere remained stable over the 10,000 years preceding the industrial revolution, that event initiated a steady increase in CO_2 levels over the past 150 years (Stevens, 2000). The resulting accumulation of CO_2 in the troposphere is increasingly linked to global climate warming, with projections of continued warming in the absence of resolute changes in CO_2 management (Revkin, 2000).

To address global warming, the Department of Energy (DoE) has initiated an extensive program to investigate the technology of capture and storage of CO_2 produced by coal fired plants. Sites now being considered for storing produced CO_2 include the deep ocean, depleted oil and gas reservoirs, deep saline aquifers, and unmineable coal beds (DoE, 2001, 2003). Although, many of these sites are believed suitable for long-term storage of CO_2, considerable uncertainties surround their permanence and how to monitor such storage sites for loss of CO_2 over centuries.

Another approach is to capture and reduce CO_2 to organic compounds including alkanes that can be reused for fuel. Reduction diverts CO_2 from the atmosphere to C_1 products and fuel and requires no large-scale storage facilities. CO_2 becomes a partly renewable resource that reduces consumption of new fossil fuels and by recycling, the rate of CO_2 production. Reduction of CO_2 is an endoergic process requiring energy input. Sunlight is an abundant though diffuse source of energy capable of effecting the reduction of CO_2 through the use of photosemiconductor catalysts such as TiO_2, $SrTiO_3$, or CdS, which form electron/hole pairs on excitation with UV or visible photons (Hoffman et al., 1995; Yoneyama, 1997). If the band gap of the semiconductor exceeds about 2 ev, the conduction-band electrons can reduce CO_2 to a variety of C_1 and C_2 products using the hydrogen in water molecules. However, intrinsic photoefficiencies (quantum yields) of photocatalysts currently used for reduction of CO_2 are very low and utilization of the solar spectrum by these catalysts is generally restricted to the UV portion of the spectrum below 400 nm, further reducing overall efficiency by up to 90% of theory.

One objective of this project is to determine how efficient existing semiconductor oxide catalysts are for reducing CO_2 using solar light and if newer photocatalysts with visible spectral absorbance have improved overall efficiency in this process. Some new photocatalysts are

claimed to split water to hydrogen and oxygen using the visible portion of the solar spectrum (Taka and Domen, 1998; Licht and Tribusch, 2000; Zou and Arakawa, 2001), suggesting they also have surface potentials suitable for reducing CO_2.

Another project objective is to develop preliminary estimates for a practical system for reduction by sunlight that uses flue gas as input CO_2. In this effort, we have determined spatial requirements (km^2) for reduction of fixed amounts of CO_2, using realistic estimates of sunlight intensity under various conditions of quantum and spectral efficiencies of the photocatalyst.

EXECUTIVE SUMMARY

The use of sunlight to reduce CO_2 to C_1 products and to fuel is being investigated as an alternative to sequestration of CO_2 in deep wells or coal beds to effectively make CO_2 a renewable energy source. A number of new photocatalysts have been reported to absorb visible light thereby improving the overall efficiency with which sunlight can be used for effecting chemical reactions and improving the competitive cost for reduction. This project has three objectives: one is to evaluate the rates and efficiencies for photoreduction of CO_2 to organic compounds using semiconductor oxides including TiO_2 and $SrTiO_3$; another objective is to examine if newer photocatalysts that absorb in the visible spectrum exhibit improved efficiency for reducing CO_2. A third objective is to develop an estimate for the cost of reducing CO_2 emitted from flue gas from a coal-fired plant using realistic estimates of sunlight intensity, reduction efficiencies and newer designs for utilizing sunlight in heterogeneous photocatalytic systems.

We investigated the photoreduction of CO_2 using a variety of oxide semiconductors and near UV light. Conventional oxide semiconductors including TiO_2 and $SrTiO_3$, as well as modified semiconductors including Pt/TiO_2 and $SrTiO_3/ Cr – Sb$, TiO_2/Fe_3O_4 and $TiO_2/Fe(CN)_6^{3-}$ were used. Analysis for formate, acetate, formaldehyde, methanol and methane were conducted by a variety of analytical methods. We found only trace quantities of formate and acetate (usually less than 1 ppm) and no clear evidence for formation of the other products.

The quantum efficiencies of TiO_2 and $SrTiO_3$ for forming formate and acetate from CO_2 is estimated to be 0.1-0.2% or less, and the overall quantum and spectral efficiencies are less than 0.01-0.02%. However, Pt/TiO_2 produced more formate and acetate than TiO_2 alone by about a factor of two. Addition of 0.6 mM 2-propanol to an irradiated CO_2/TiO_2 suspension led to formation of 0.55 mM (25 ppm) formate, probably because re-oxidation of formate by semiconductor holes was competitively blocked by propanol acting as an electron donor. Formate is oxidized by TiO_2 under argon 80 times faster than CO_2 is reduced. Thus, reoxidation may be an important process limiting the accumulation of products and will require new design strategies for reducing accumulation of products in the photocatalytic zone if the an efficient process is to be developed.

Preliminary estimates give the physical size of a 100% efficient solar CO_2 photoreduction unit large enough to reduce the CO_2 produced from a 1000 MW coal-fired

electricity plant as about 10 km^2. Realistic estimates place the size closer to 50-200 km^2. New much more efficient photocatalysts need to be discovered to make photoreduction of CO_2 a practical process for recycling significant quantities of fossil fuel-derived CO_2.

EXPERIMENTAL

ANALYTICAL METHODS

Carbon Dioxide Sensor and Reactor

A CO_2 infrared sensor (Vaisala, Woburn, MA, Model GMM221) with a sensor card were assembled with a power source and voltmeter readout to detect gas phase CO_2 released from the aqueous HCO_3^- solutions. The sensor is designed to detect gaseous CO_2 in concentrations from 10 ppm to 50,000 ppm (0.5%). A borosilicate glass reactor was designed to house the cylindrical sensor above a solution of sulfuric acid into which small aliquots of the photolyzed HCO_3^-/photocatalyst mixture are injected. The CO_2, released from the acidic solution mixes with argon previously used to flush air from the reactor, is measured by the sensor and the amount is read out from a voltmeter. The reactor with sensor was calibrated with known amounts of HCO_3^- solutions over the range of 0 to 0.04 mM. The reproducibility of the sensor is rated at $\pm 2\%$. Reaction aliquots of 0.1 mL solution were injected into 2 mL stirred 1.0 M H_2SO_4 solution in a sealed glass vessel previously swept with argon (100 mL/min) for 5 min. Sensor readouts to a voltmeter were calibrated using standard solutions of 0.05 to 0.4 M $NaHCO_3$. A calibration curve for CO_2 including a zero value is shown in Figure 1. The drop off at 0.05 M CO_2 may reflect the unfavorable partitioning of CO_2 between aqueous and gas phases at low CO_2 concentrations.

Formaldehyde Measurements

The Nash colorimetric method (Nash, 1953) has been used by a number of workers to determine formaldehyde (CH_2O) and formic acid in photoreaction mixtures (Ulman et al., 1982; Sharma et al., 1997). We prepared the calibration curve for formaldehyde using 33% formalin solution diluted to the μM range with Milli Q water. Dilute CH_2O solutions (0.8 mL) were mixed with 0.5 mL Nash reagent (prepared from 150 g ammonium acetate, 3 mL acetic acid, and 2 mL acetylacetone diluted to 1 L with Milli Q water) and allowed to stand for 90 minutes. A series of CH_2O-Nash reagent mixtures with concentrations ranging from 0.033 to 6.67 μM CH_2O were analyzed by UV/VIS spectrophotometry at 412 nm. The calibration curve is shown in Figure 2.
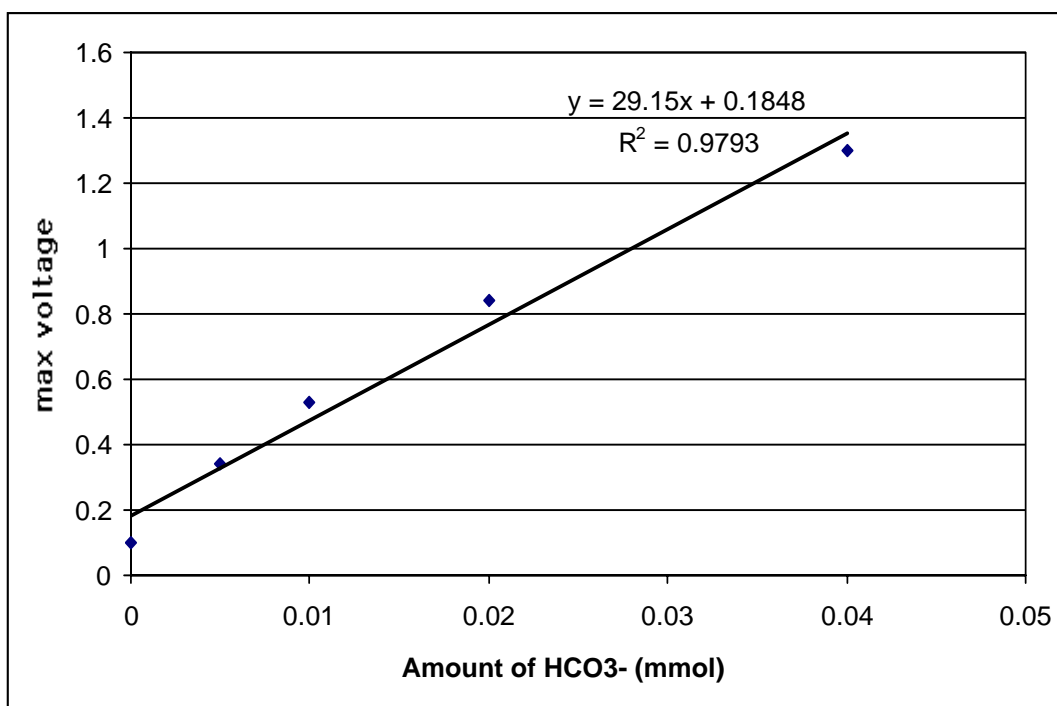
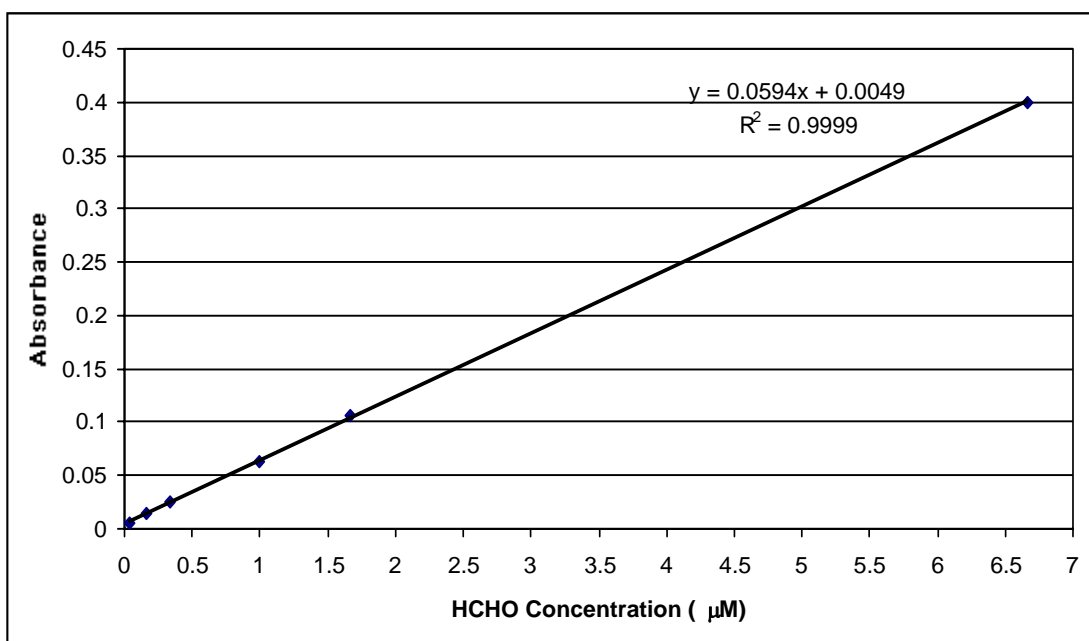Figure 1. Bicarbonate ion calibration using the IR sensor.

Figure 2. Formaldehyde calibration using the Nash reagent. Absorbances were measured after 90 minutes.

Methane and Methanol Analyses

Methanol and methane analyses were carried out using a SRI Instruments (Torrance, CA) dual oven 8610 chromatograph equipped with a FI detector operating with 250 mL/min air and 27 mL/min H_2. Separation of methanol from water was accomplished on a Poroplot Q Chrompak wide-bore capillary column (Varian), 25 m x 0.53 mm operating with 25 mL/min N_2 flow. Elution time for methanol was 3.2 min in a temperature programmed cycle from 80 to 170°C over 6 min. Water produces a false peak and tail starting at 2.1 min, but 5 µL of 325 µM (10 ppm) methanol produces a large peak on the tail. Injections of 5 µL of 65 µM (2 ppm) methanol under these conditions produces a distinct peak, but 30 µM does not.

Methane analysis used the same column but a different programming cycle from 50-125° in 7.5 min. Under these conditions, methane elutes at 1.59 min. Gas injections of 0.5–1.0 mL of methane standards with 10 to 10,000 ppm methane in CO_2 were used to calibrate the response. Background methane in CO_2 is about 1 ppm, limiting detectability in reaction mixtures.

Formate Analysis by Capillary Ion Analysis (CIA)

CIA, an alternative analytical method for low concentration anions is based on electrophoretic separation. When optimized, the method can be used to detect a wide range of anions in the >20 µm (>1 ppm) concentration range. The detection method depends on the displacement by the anion of a proprietary mobile phase, which absorbs in the UV spectrum at 254 nm; hence, the improved sensitivity over HPLC, which depends on direct UV absorption by the anions around 210 nm.

CIA were conducted with a Waters Quanta 4000 Capillary Ion Analyzer (Waters, Franklin, MA) using a 75 µm x 60 cm fused silica capillary column and a pH 5.6, 0.05 molar phthalate buffer with Waters osmotic flow modifier as the electrolyte. Detection is based on indirect UV absorption at 254 nm. Migration times (approximate) of anions in a standard mixture of 10 ppm each of thiocyanate (internal standard), formate, acetate, oxalate, and bicarbonate are 3.1, 3.22, 3.6, 2.85, and 4.2 min, respectively, at 25°C. The instrument acquired data at the rate of 20 bits/s and integrated peak areas in the time corrected mode. Reproducibility of time corrected peak areas for a standard mixture of 10 ppm of thiocyanate (0.17 mM) and 2 ppm (44 µM) formate ions in a series of replicate runs conducted on the same day was good: for thiocyanate the peak area was 429 ± 11; formate peak area was 345 ± 11 or about a standard deviation $\pm 3\%$ in both cases. Figure 3 shows a typical CIA plot for thiocyanate and formate.
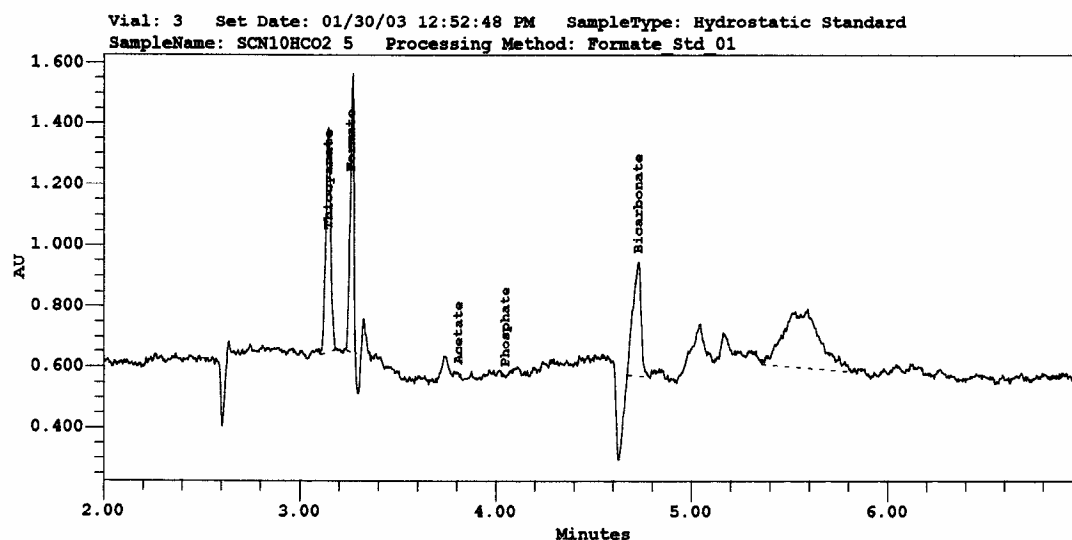
Figure 3. CIA plot for analysis of 10 ppm thiocyanate and 2 ppm formate ions.

Although the detectability of formate by CIA in mixtures was close to 10 μM (420 ppb or 0.42 μg/mL) under ideal conditions, after correcting for background, day to day reproducibility of the instrument is only fair with peak areas changing by as much as 20 to 25%. To account for this variability, all CIA analyses are conducted with standard mixtures of thiocyanate and formate ions. In practice, we could never detect formate or acetate by CIA reliably much below concentrations of 22 and 17 μM, respectively (1 ppm).

Formate and Acetate Analysis by Ion Chromatography

Ion chromatographic (IC) analyses for formate and acetate were conducted by West Coast Analytical Services (WCAS) in Santa Fe Springs, CA. The IC method can detect formate and acetate reliably to 0.22 and 0.17 μM (10 ppb), or about 100 times lower concentration than CIA. The WCAS IC analytical method gave retention times for formate and acetate ion of 6.63 and 5.30 min, respectively, with peak areas of 100,000 for each 2 μM formate. WCAS claims reproducibility of $\pm$0.5% on peak areas of 25000 or larger.

MATERIALS AND SUPPLIES

All of the chemicals are reagent grade and were used as is. A sample of P-25 anatase TiO_2 was obtained from DeGussa (DeGussa Corporation, Cameron, NJ) and anatase TiO_2 and $SrTiO_3$ were purchased from Alfa Aesar (Ward Hill, MA) as high surface powders with

8

estimated particle sizes of 30 to 50 nm; both powders are bright white. $SrTiO_3$, doped with Cr and Sb was prepared by sintering a mixture of $SrCO_3$, TiO_2 with Cr_2O_3, and Sb_2O_3 at 1100°C for 30 hours in an alumina boat (Hirano et al., 2000). The resultant powder is tan colored. Hematite-coated TiO_2 was prepared from titanium tetrabutoxide (Ti(OBu) $_4$) and hematite particles following the procedure of Penpolcharoen et al. (1998). The dry catalyst is an ochre-colored fine powder. CO_2 gas is purified by passing it successively through concentrated sulfuric acid and pure water using gas-washing bottles fitted with fritted outlets. Platinized TiO_2 was prepared by the method of Kim and Choi (2002). The gray powder is estimated to have 2% Pt deposited on the TiO_2 particles.

PHOTOCHEMICAL METHODS

Light Source and Photoreactors

The light source for these experiments is a Varian/EIMAC air-cooled 300 w xenon lamp. A 2-cm diameter borosilicate glass cylinder or a 10 cm diameter borosilicate bottle filled with pure water was positioned directly in the light beam to remove UV light below 300 nm and IR light above 1200 nm.

Light intensity from the xenon lamp was measured using two different actinometer solutions in the same reactor tubes used for CO_2 reductions. One actinometer is 10 μM aqueous ammonium dinitramide (ADN, Yao et al., 1995). ADN has a broad absorption band from 260 to 360 nm and photolyzes rapidly in uv light with a quantum efficiency of 10% to give products, which do not absorb in the near UV. Loss of ADN was monitored by the loss of absorption at the peak maximum at 284 nm. The half-life for ADN was found to be 140 sec in borosilicate tubes and 110 sec in quartz tubes. For comparison, ADN has a half-life in sunlight in quartz tubes in late winter of 240 sec (Mill, 2002). In other words, the xenon source produces about twice the near UV photon flux of winter sunlight under our experimental conditions. We did not use ADN to estimate the light flux in our laboratory experiments because of the relatively large errors associated with using optically thin actinometers such as ADN to estimate broad band radiation intensities, compared with using optically thick actinometers such as azoxybenzene (Bunce et al., 1984) or potassium ferrioxalate (Calvert and Pitts, 1966).

Five mM azoxybenzene (AZB) in ethanol absorbs light strongly (>98%) from 400 nm into the far UV and forms 2-hydroxyazobenzene on irradiation anywhere in the absorption band with a quantum efficiency of 20%. The product is readily measured by its strong absorption as the anion at 458 nm. AZB solutions in the 300 mL reactor were irradiated for up to 900 sec

9

while samples were withdrawn at 10 to 300 sec intervals, basified with KOH solution and analyzed by UV. The method of Bunce et al. (1984) was used to plot the data and estimate photon fluxes in the photoreactor.

The photoreactors used in these experiments are either 20 mL borosilicate cylindrical tubes (1.5 cm path), 100 mL quartz cylindrical tubes (2 cm path), or 160 mL borosilicate serum bottles (5 cm path). All of the reactors were fitted with serum stoppers and/or closure valves and the contents of the reactors were magnetically stirred.

Photoreaction Procedures

In a typical procedure, 10 to 100 mL of Milli Q water was placed in a reactor with a weighed amount of catalyst to give a 0.1 to 0.15% by weight suspension and was rapidly stirred at 25°C, while a stream of CO_2 gas was introduced at the bottom of the reactor with a 10 to 20 cm long No. 20 hypodermic needle inserted through the serum stopper. A No. 24 needle served as the outflow. After 30 to 40 min of rapid stirring and sparging, an aliquot is removed through the septum as a control, the inflow needle was either moved up into the gas phase and the CO_2 flow continued for the duration of the experiment after the lamp was turned on or the needles were removed and the reactor was sealed under CO_2 for the duration of the experiment. In experiments using HCO_3^- instead of CO_2, argon was bubbled through a serum-stoppered reactor solution using syringe needles for 30 to 50 minutes to remove air. Both the controls and the reaction aliquots were filtered through 0.45-μm syringe filters to remove catalyst particles; the solutions were then ready for product analyses.

Sunlight experiments with 0.15% $SrTiO_3$ and Pt/TiO_2 suspensions in CO_2-saturated water were conducted in 100 mL sealed quartz tubes under CO_2, suspended outdoors at about 40° from horizontal, facing south and magnetically stirred for 28 hours, corresponding to about 18 hours of sunlight in late May at San Francisco (38° N Lat).

BACKGROUND, EXPERIMENTAL RESULTS, AND DISCUSSION

PUBLISHED STUDIES

Several dozen papers have been published in the past 30 years describing reduction of CO_2 by semiconductor oxide photocatalysts such as TiO_2 to form a variety of C_1–C_4 products. Some of this work was reviewed by Yoneyama in 1997 and by Halman and Steinberg in 1999. In most cases, yields of products were in the μM range. Our strategy for this project was to start with catalysts, conditions, and methods used previously to give formate, formaldehyde, and methanol from CO_2 in photocatalyzed reactions and to repeat them and measure their quantum efficiencies as well as major products.

Table 1 summarizes published accounts of reduction products from CO_2 using a variety of photocatalysts such as TiO_2, $SrTiO_3$, CdS, and Cu on silicate rock and even the organic dye toluidine blue. Some workers used far UV light, some near UV or solar UV light and in two cases, tungsten lamps were used with visible light- absorbing catalysts. Irradiation times varied from 120 min to 30 hours. Some experiments used bicarbonate ion, others used flowing or static CO_2 in water. Formate and formaldehyde are reported in many of these experiments as are methane and methanol, but in significantly different concentrations when corrected for differences in times and volumes.

For example, formate yields are reported as 28 μM in 24 hrs (1 μM/hr) using $SrTiO_3$ as a photocatalyst with a mercury lamp (UV light) and flowing CO_2 gas (Irvine et al., 1990) and 185 μM in 150 min (1.2 μM/min) using TiO_2 with a xenon lamp, bicarbonate ion, and oxalate ion as an electron donor (Goren et al., 1990). Sayama et al. (1993) used ZrO_2 and found no formate, only CO. Sharma et al. (1997) used ferrocyanide-modified TiO_2 and claims to have made 2.9 mM formate in 100 min (29 μM/min) with a tungsten (visible light) bulb. Sharma et al. also showed that at longer times formate slowly disappeared, presumably reflecting both further reduction as well as reoxidation to CO_2. Some workers assert that TiO_2 alone does not reduce CO_2. However, Ikeue et al. (1993) report finding methanol and methane using TiO_2/SiO_2 and Mizuno et al. (1996) report finding formate with TiO_2 alone.

Table 1. Reported Products from CO_2 Photoreduction

Catalysts	Products	Concentrations	Light Sources	Conditions/Times	Citation
TiO_2/Pd TiO_2	HCO_2H HCO_2H	8.3 μM/100 min 1.3 μM/100 min	450 W Xenon >360 nm	3 mL 0.05 M $NaHCO_3$ 0.05 M oxalate	Goren et al., 1990
TiO_2	HCOOH CH_3OH	2 μM 12 μM	4.5 kW Xenon lamp	0.1 to 2.5 MPa CO_2 in water	Mizuno et al., 1996
TiO_2/SiO_2	CH_4 CH_3OH	7 μM[a] 2 μM[a]	High pressure Hg lamp	36 μM CO_2 180 μM H_2O gas phase	Ikeue et al., 2002
TiO_2/Metals	CH_4 CH_3COOH	0.2 μM/Pd 0.05 μM/Rh	500 W Hg lamp	150 mg/mL[b]	Ishitani et al., 1993
TiO_2 ZnO GaP	HCHO CH_3OH	1-2 mM 3-14 mM	500 W Xenon lamp	1 g/100 mL[b] CO_2 flow 7-30 h	Miyasaka et al., 1979
TiO_2/Fe(CN$_6^{4-}$	HCOOH H_2CO	29 μM/100 min 0.66 μM/100 min	500 W Tungsten	1 g/150 mL[b] CO_2 flow 210 min	Sharma et al., 1997
$SrTiO_3$	HCO_2H H_2CO MeOH CH_3CHO	7.5 μM/h 0.31 μM/h 0.13 μM/h <0.06 μM/h	75 W Hg lamp (high p), 1 g	1 g/160 mL[b] CO_2 flow at 100 mL/min 60°C	Ulman et al., 1982
CdS ZnO $SrTiO_3$	HCO_2H, H_2CO HCO_2H H_2CO	28 μM, 2.3 μM 24 μM 5 μM	High pressure Hg lamp with borosilicate or quartz	0.15 g/50 mL[b] CO_2 flow 24 hr	Irvine et al., 1990
ZrO_2	CO	8.6 μM/h	400 W Hg lamp quartz	1 g/350 mL[b] 0.33 M $NaHCO_3$	Sayama and Arakawa, 1993
$CaFe_2O_4$	H_2CO CH_3OH	38 μM 8.2 μM	High pressure Hg lamp	0.3 g/60 mL[b] 0.01 M NaCH CO_2 saturated 4 hr	Matsumoto et al., 1993
Cu/SiO_2	HCOOH	10 μM	Sunlight, borosilicate	5 g/5 mL CO_2[b] (no flow) 10 hr	Ohta et al., 1998
Toluidine Blue 1 (-4) M	HCOOH H_2CO	220 μM 62 μM	500 W Tungsten	50 mL 1 mM $CO_3^=$ no pH effect 120 min	Jain et al., 2001

[a] μM/gTiO_2h
[b] Grams catalyst/volume solution

PHOTOREDUCTION EXPERIMENTS

To evaluate these published experiments, we tested and standardized analytical methods for detecting formate, acetate, formaldehyde, methanol and methane. In early experiments, we also measured CO_2 lost by reduction, but when it became apparent that reactions produced no more than low micromolar concentrations of products, we stopped. The initial concentration of CO_2 in nonbuffered water is about 0.03 M (Butler, 1981), so changes on the order of 10^{-4} of this concentration would be undetectable.

Initial photocatalyzed reduction experiments were conducted using 0.1 or 0.15% anatase TiO_2 and $SrTiO_3$ in the presence of HCO_3^- ion in an effort to reproduce work shown in Table 1 (Miyasaka et al., 1979; Goren et al., 1990; Ulman et al., 1982; Mizuno et al., 1996). We followed both loss of HCO_3^- ion from solution and formation of formate and formaldehyde. Although loss of HCO_3^- ion indicated significant reduction of CO_2, we were unable to find products using the HPLC or CIA for formate and acetate and the Nash method for formaldehyde. Only later when we switched to the IC method for anion analysis did we detect formate and acetate ions, but only in sub-ppm concentrations. Formaldehyde, if it forms at all, appears to be present at concentrations close to background values and is indistinguishable from it.

Initial reaction mixtures used 0.1 M aqueous HCO_3^- ion solution. To use CIA to analyze for acids, excess HCO_3^- had to be removed prior to analysis, an uncertain process. Therefore, we switched to CO_2 gas to saturate solutions at pH~7 and removed excess CO_2 after reaction by brief vacuum treatment. Once IC analysis was used for formate and acetate, CO_2 removal was unnecessary.

Table 2 summarizes results from some of the experiments conducted with several oxide semiconductor catalysts and mostly with CO_2-saturated water in artificial and real sunlight. Except for the one case where 2-propanol was added, these experiments produced concentrations of formate, acetate or formaldehyde below 1 ppm and were detectable only by IC (for the acids). No methane or methanol were reliably detected in any experiments and most experiments shown in Table 2 were run in duplicate or triplicate.

The simplest system is one using only TiO_2 and CO_2. Experiments 2 and 11 were conducted in similar ways. However while Experiment 2 gave no evidence for product formation using CIA analysis, Experiment 11 using IC analysis was found to have formed products in sub ppm concentrations. Experiments 8/9 and 10/11 with Pt/TiO_2 and $SrTiO_3$ show that although about twice as much acetate as formate forms with artificial and real sunlight, the absolute yields

13

Table 2. Experiments on Photoreduction of CO_2

Experiment No.	Catalyst (% Loading)	Conditions[a]	Time, h	Products[b]
1	$SrTiO_3$ (0.10)	0.1 M HCO_3^-	24	Formate, present in control, decreased
2	TiO_2 (0.15)	CO_2 flow	24	No formate detected by CIA No CH_2O detected
3	TiO_2 (0.15)	0.440 mM HCO_2^- under argon	25	320 μM Formate consumed No CH_2O
4	$SrTiO_3$ (0.15)	CO_2 flow 0.67 mM 2-PrOH	24	Formate 22 μM (1 ppm) No CH_2O detected
5	$SrTiO_3$ (0.15)	CO_2 flow 0.75 mM NaOH	24	No CH_3OH No formate No CH_2O
6	$SrTiO_3$ (0.15)	CO_2 static 0.75 mM NaOH	24	No formate or CH_2O
7	$SrTiO_3$ (0.1)	CO_2 flow 0.67 mM 2-PrOH 0.75 mM NaOH	20	No formate
8	Pt/TiO_2 (0.15)	CO_2 flow	6	Formate 12 μM (0.54 ppm) Acetate 20 μM (1.3 ppm)
9	$SrTiO_3$ (0.15)	CO_2 flow	6	Formate 2.9 μM (0.13 ppm) Acetate 5 μM (0.30 ppm)
10	$SrTiO_3$ (SbO_x CrO_y) (0.15)	CO_2 flow	24	No formate or acetate by CIA, no CH_4 or CH_3OH
11	TiO_2 (0.10)	CO_2 flow	22	Formate 4 μM (0.19 ppm) Acetate 7 μM (0.45 ppm) No CH_4 or CH_2O
12	Pt/TiO_2 (0.15)	CO_2 static sunlight	18[c]	Formate 5.1 μM (0.23 ppm) Acetate 8.5 μM (0.50 ppm); no MeOH
13	$SrTiO_3$ (0.15)	CO_2 static sunlight	18[c]	Formate 18 μM (0.81 ppm) Acetate 29 μM (1.7) ppm
14	TiO_2/Fe_3O_4 (0.1)	CO_2 static	23	No acids detected No formaldehyde detected
15	$TiO_2/Fe(CN)_6^{3-}$ (0.1)	CO_2 static	19	Formate <22 μM (1 ppm) Acetate <4.2 μM (2.5 ppm)

[a]Irradiated with 300 w xenon source at 25 cm.
[b]Detection limits for HCO_2^- and CH_2O are 2 and 5 μM.
[c]Sunlight hrs.

14

are similar for each acid if differences in photon fluxes are taken into account. With both sources, product formation was very slow, about 2 to 3 μM/hr with the artificial light and 0.3 to 1 μM/hr in sunlight with its more variable intensity. The experiments also show that Pt/TiO_2 consistently produces higher rates of product formation,by a factor of about 3 to 4 compared with TiO_2 or $SrTiO_3$ (8 versus 9 or 10 and 12 versus 13). Possibly, the greater effectiveness of Pt/TiO_2 is simply because the gray Pt/TiO_2 powder absorbs more visible light than bright white $SrTiO_3$ or TiO_2 (but see below).

Experiments 14 and 15 used TiO_2 coated or sorbed with iron complexes—in one case the oxide and on the other ferricyanide. In neither case could we reliably find products above the detectability limits of the analytical methods. Both TiO_2-iron catalysts absorbed visible light (both were yellow-brown), but neither exhibited any reducing activity. Sharma et al. claimed high reactivity for the ferricyanide coated TiO_2 for producing formate from a result we were unable to duplicate with a catalyst prepared using their procedure.

Experiment 3 started with a mixture of 440 μM formate under argon with TiO_2 and resulted in loss of most of the formate during 24 hours irradiation, demonstrating how oxidizable formate is in this system and that the light source was producing significant amounts of near UV light. Two experiments (4 and 7) were carried out with added 2-propanol as an electron donor to enhance yields of formate and formaldehyde by inhibiting their reoxidation to CO_2 by semiconductor holes (h_{VB}^+). In one experiment (Experiment 4), addition of 0.67 mM (40 ppm) 2-propanol did lead to formation of a measurable amount of formate (22 μM, 1 ppm); however, experiment (7) with propanol did not give any detectable amount of formate when NaOH was added.

One series of experiments with 0.1% $SrTiO_3$ suspension saturated with CO_2 examined the time dependence of formation of formate and acetate over 31 hours. Results, summarized in Table 3, show a progressive increase in acetate starting at 8 hours, but formate does not appear until 19 hours and oxalate was detected only at 31 hours. No methanol was detected in any experiment.

To evaluate the reoxidation of formate by semiconductor holes as an explanation for the low rates of production, we irradiated 0.440 mM (19 ppm) formate under argon with 0.15% TiO_2 (Experiment 3). After 20 hours, 70% of the original formate had disappeared (0.31 mM), but because no formaldehyde was detected (above 5 μM), we conclude that reoxidation is the most likely explanation for the loss. Sharma et al. (1997) noted that the production of formate declined after 90 minutes irradiation, with a parallel loss of formaldehyde, providing some possible additional evidence that re-oxidation to CO_2 can be an important loss process for C_1

products. On the other hand, the time series experiments shown in Table 3 show a buildup of formate and acetate over the 31 hours time course of the experiment, although at no time did the apparent concentrations exceed about 30 µM formate and 9 µM acetate.

Table 3. Results from Experiment 16: Time Dependent SrTiO$_3$ Irradiation of CO$_2$-Saturated MQW[a]

Sample Time, hr	Formate, µM (ppm)	Acetate, µM (ppm)	Oxalate, µM (ppm)	MeOH, µM (ppm)
0	ND	ND	-	ND
3	ND	ND	-	ND
8	ND	4.5 (0.26)	-	ND
19	24 (1.1)	6.2 (0.36)	-	ND
31	30 (1.4)	9.0 (0.53)	0.7 (0.06)	ND

[a]A 100 mL suspension of 0.1 % SrTiO$_3$ was illuminated with a 300 W filtered xenon source while CO$_2$ was bubbled through. Acids were analyzed by IC.

PHOTOEFFICIENCY

Several experiments were conducted expressly to measure light intensity (I$_0$) incident on the inside of the borosilicate reactor window and, from that information, to estimate quantum efficiencies for TiO$_2$ and SrTiO$_3$ in converting CO$_2$ to products. We measured I$_0$ by filling the reactor with a chemical actinometer, 5 mM azoxybenzene (AZB), which absorbs all light below 400 nm, and measuring the rate of conversion of AZB to 2-hydroxyazobenzene over a measured time interval of about 15 min. That information, coupled with the measured quantum efficiency for AZB's conversion to hydroxyazobenzene of about 2% (Bunce et al., 1984), provides a value for I$_0$.

One complication in the procedure is caused by the fact that although 5 mM AZB absorbs all light below 400 nm, 0.1% TiO$_2$ and SrTiO$_3$ suspensions absorb UV light strongly (90%) only below about 350 nm (Figure 4). To correct our measurements for this difference in absorption by AZB and TiO$_2$, a cutoff filter was used in one actinometer experiment to remove light below 350 nm. In the other experiment without a filter, all light between 400 nm and 300 nm (the cutoff for the borosilicate reactor) was collected by AZB. By subtracting the measured values of I$_0$ in the experiments, a value of I$_0$ for the spectral region between 300 and 350 nm was obtained, which is similar to the UV region in which the photocatalysts absorb light:
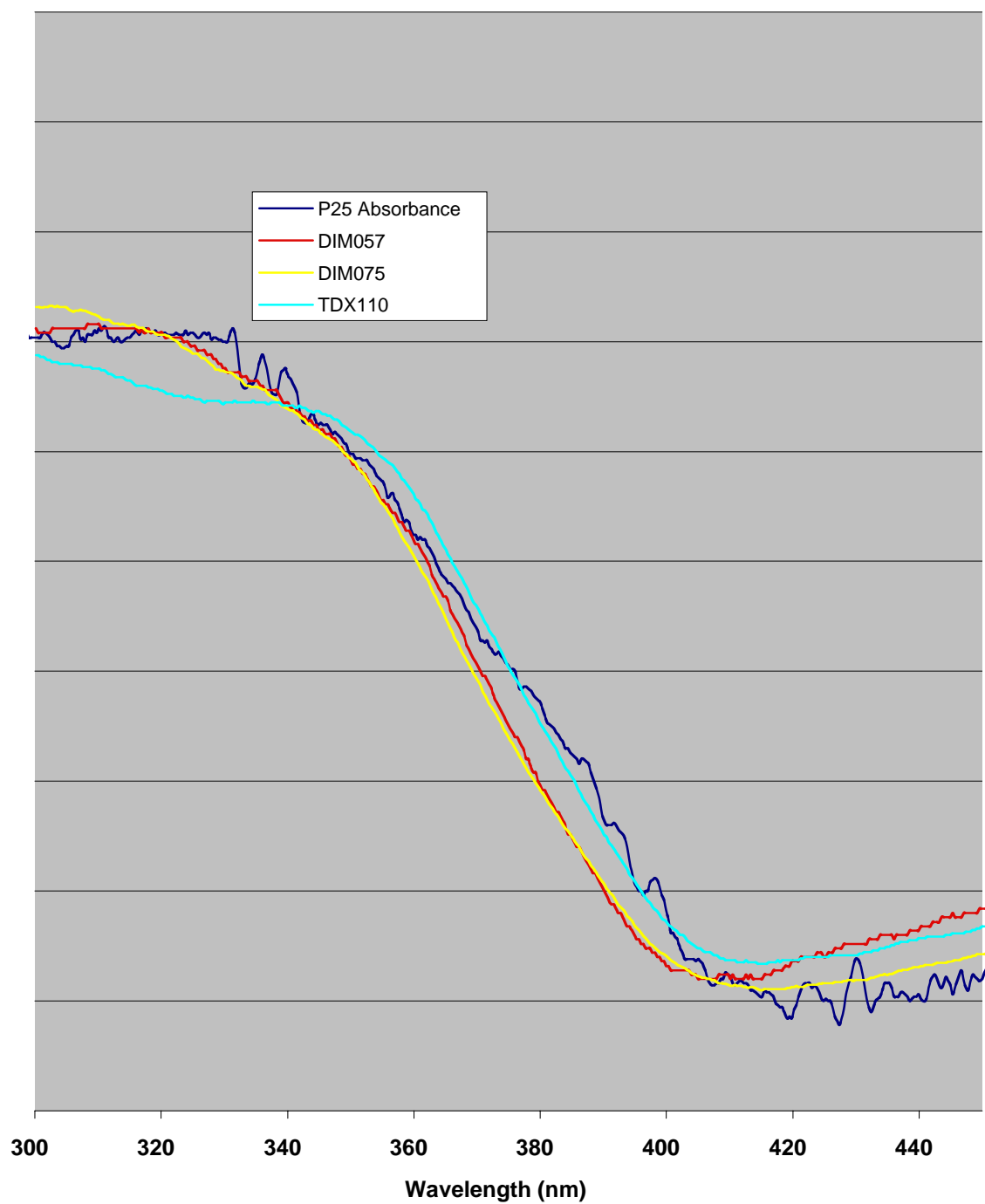
16

Titania Absorbance Spectra

Figure 4. Absorbance spectra for TiO_2 powders

$$I_0(300\text{-}400) = 1.25 \times 10^{-6} \ \text{E/Ls}$$

$$I_0(350\text{-}400) = 5.89 \times 10^{-7} \ \text{E/Ls}$$

$$I_0(300\text{-}350) = 6.60 \times 10^{-7} \ \text{E/Ls}$$

An estimate of the quantum yield for production of 4×10^{-6} M (0.19 ppm) formate formed over 22 hours in a 100 mL volume (Experiment 11) is given by the ratio of formate formed to the 5.2×10^{-2} moles of photons (Einsteins) absorbed over 22 hours in this experiment. The apparent quantum yield for this reaction is

$$\phi = 4 \times 10^{-6}/5.2 \times 10^{-2} = 7.7 \times 10^{-5}$$

When the requirement of two photons per formate is taken into account, this value is equivalent to 0.015% efficiency. When acetate formation in the experiment (7×10^{-6} M) is included in the estimate, the efficiency for producing both of these compounds increases to

$$\phi = [4 \times 10^{-6}/5.2 \times 10^{-2}] + [7 \times 10^{-6}/5.2 \times 10^{-2}] = 2.1 \times 10^{-4}$$

When this value is corrected for the numbers of photons required for formation of formate (2) and acetate (8), the quantum efficiency increases to 1.2×10^{-3} or 0.1%, still a low efficiency process. If reliable measurements for methanol or methane were available those values would be added to this value to improve the overall quantum efficiency. Unfortunately there is no compelling evidence for their formation in amounts that would significantly change the low values estimated here.
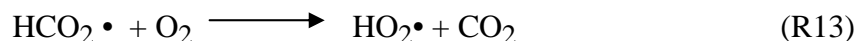
A similar calculation for the quantum efficiency for $SrTiO_3$ in experiment 9 gives the quantum efficiency for forming formate of close to 0.035%, roughly twice the value for TiO_2. This estimate assumes that $SrTiO_3$ absorbs UV light in a manner similar to TiO_2 and has an onset for absorption of UV light close to 350 nm.

Experiment 3 uses the same catalyst to oxidize formate under argon with a quantum efficiency that can be estimated in the same manner as the for the reductions, assuming the value of I_0 in this experiment (25 hr) is similar to that in the reduction experiments:

$$\phi(\text{oxid}) = 3.2 \times 10^{-4}/5.9 \times 10^{-2} = 5.4 \times 10^{-3}$$

The efficiency for oxidation in argon is about eighty times larger than for reduction. Cornu et al (2001) report a quantum yield for formate oxidation by TiO_2 in oxygen of about 0.02 (2%), or about 3 times higher than for oxidation in argon. The difference may reflect the reversibility of the hole oxidation of formate when no H$^-$ atom scavenger is available such as oxygen

$$h_{VB}^{+} + HCO_2^{-} \longrightarrow HCO_2 \bullet \qquad\qquad (R11)$$

$$HCO_2 \bullet \; \rightleftharpoons \; CO_2 + H\bullet \qquad\qquad\qquad (R12)$$

$$HCO_2 \bullet + O_2 \; \longrightarrow \; HO_2\bullet + CO_2 \qquad\qquad\qquad (R13)$$

SPATIAL ESTIMATES FOR A SOLAR PHOTOREDUCTION UNIT

The spatial requirements for solar reduction of CO_2 produced from a power source can be estimated by starting with the photon flux incident on the Earth's surface at some geographically and seasonally defined location. Tables of solar insolation data list sunlight irradiance (mE/cm^2 day) as function of latitude (0°-70°) and season and for the spectral region from 295 to 800 nm under clear skies (Zepp and Cline, 1977; Mill et al., 1982; Leifer 1988). For 40° latitude and summer, the photon flux from 295-800 nm is about 9.73 mEinsteins/cm^2 per 24 hour day under clear sky conditions. Figure 5 illustrates the total photon flux per day for the full solar spectrum and for abbreviated portions of the spectrum.

Irradiance values (as L_λ) are computed for a 24-day to even out diurnal variations in solar irradiance during daylight hours. Mid-summer days at 40° latitude are close to 14 hours long (geoastro, 1999). Actual irradiance values are therefore 1.7 times larger (on average) than L_λ values shown in Figure 5. However, because photoreduction rates drop to zero during twilight and nighttime hours, the actual net reduction of CO_2 per 24-hour day remains the same.
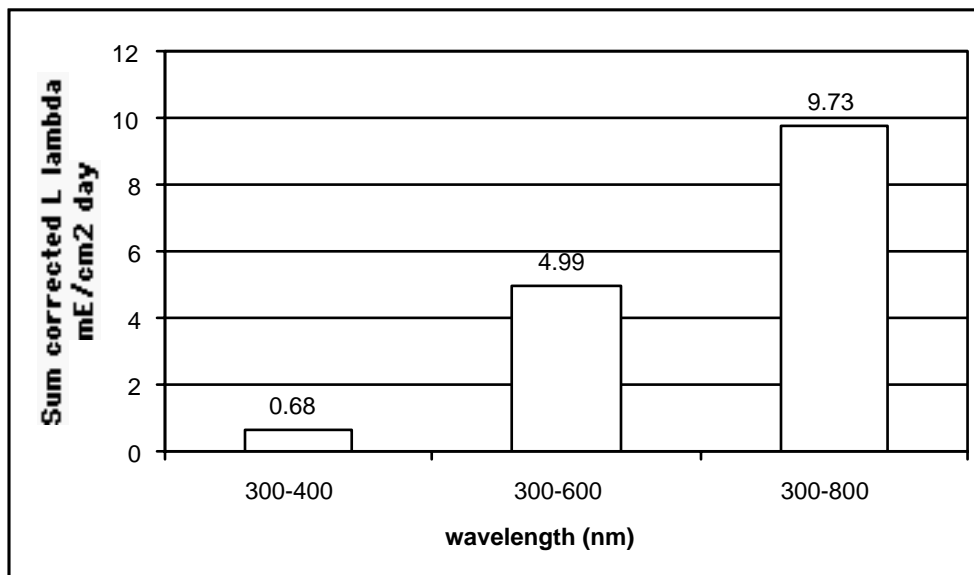

Figure 5. Total sunlight photon flux in mE/cm^2 day as a function of wavelength range.

Additional assumptions used in the calculation are that the photoefficiency of reduction of CO_2 to formate is 100% and the intrinsic quantum yield is 0.5 because of the requirement for two photons (electrons) per CO_2 to form formate.

A 1000-MW coal-fired electric plant using 70% carbon coal with 40% efficiency produces about 22000 metric tons of CO_2 per day (Halmann and Steinberg, 1999) or 4.9×10^8 moles of CO_2. Perfect efficiency in reduction of CO_2 to formate will require $\sim 1 \times 10^9$ moles of photons (einsteins)/day. Therefore, the spatial requirement will be

$$1 \times 10^9 \text{ einsteins/day}/9.7 \times 10^{-3} \text{ einsteins/cm}^2 \text{ day} = 1 \times 10^{11} \text{ cm}^2$$

$$1 \times 10^{11} \text{ cm}^2 = 10 \text{ km}^2$$

If the quantum yield for formation is only 0.05 (5%), the spatial requirement will increase by 10 to 100 km^2. If only half the CO_2 produced is to be reduced (only during daylight hours), the spatial requirement is reduced by about half. If the catalyst absorbs sunlight only to 600 nm or has a limiting redox potential equivalent in energy to 600 nm (see below), the photon flux decreases to 5 meinsteins/cm^2 day, thereby increasing the spatial requirement by a factor of almost two.

This simplistic analysis only gives a first order estimate of the minimum surface area needed to collect sufficient solar photons to effect reduction of all or part of the CO_2 produced in a large coal-fired plant. If the actual efficiency of a practical solar collector times the quantum and spectral efficiency of an optimized photoreduction process is no greater than 5-10%, the spatial requirement increases to 100-200 km^2, a site roughly 5 miles by 5 miles. Because we have used summer sunlight and clear sky intensities for this estimate, it is obvious that any practical process must have a very high quantum efficiency over a broad swath of the solar spectrum and the design of the actual unit components must ensure very high efficiency in capturing sunlight photons for the reduction process. The photoreduction capacity of any solar-based system probably is not capable of handling the entire output of a large-scale fossil fuel electricity plant.

DISCUSSION

Thermodynamic estimates for the concentration of formate in equilibrium with CO_2 at pH 7 would require an enormous pressure of CO_2- in excess of 10^{35} bars- to produce measurable quantities of formate, indicating the need for an external chemical or energy source to drive the reduction. The simplified key reactions for photocatalyzed reduction of CO_2 to organic compounds such as formate are
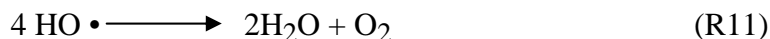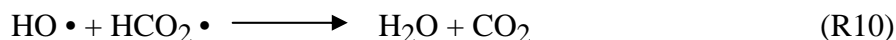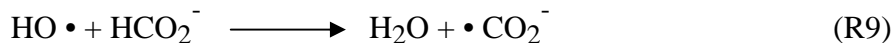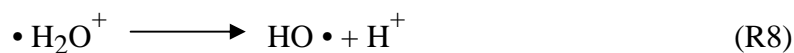
$$TiO_2 + h\nu \rightarrow TiO_2[e_{CB}^- + h_{VB}^+] \tag{R1}$$

$$TiO_2[e_{CB}^- + h_{VB}^+] \rightarrow TiO_2 + heat \tag{R2}$$

$$H_2O + h_{VB}^+ \rightarrow HO + H^+ \tag{R3}$$

$$CO_2 + 2\ e_{CB}^- + 2H^+ \rightarrow HCOOH \tag{R4}$$
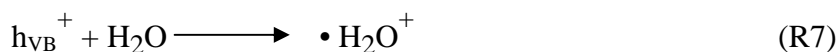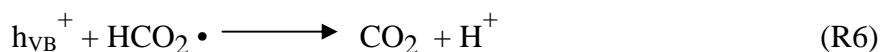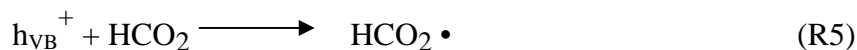
where e_{CB}^- and h_{VB}^+ are the conduction band electron and valence band hole charge carriers, respectively, generated by absorption of a photon by the semiconductor (R1). The redox potential for reaction (R4) is–0.42 V, very close to the potential for water reduction to H_2 (-0.41 V), or about 2 eV or 620 nm (Goren et al., 1990). R2, the recombination of charge carriers with heat formation, is very likely the chief source of inefficiency in the semiconductor-catalyzed process (Lewis, 1998; Upadhya et al., 1997).

Published quantum efficiencies [(product moles/einsteins photons) x 100] for formate formation from CO_2 are relatively few. Ikeue et al. ((2002) report values as high as 0.28% for methane and methanol formation from gas phase CO_2 using a Ti-containing thin film porous silica catalyst; they also report an efficiency of 0.02% using another silica-based TiO_2 catalyst, showing how variable the efficiencies for this process can be even using the same oxide photocatalyst. Henglein (1984) report quantum efficiencies of 80% for reduction of CO_2 using ZnO with $SO_3^=$ ion as electron donor. Inoue et al. (1990) claim that ZnS also gave high efficiencies (30%) in the same reduction, but with 2-propanol instead of $SO_3^=$. However, Kisch and Twardzik (1991) found only 0.1% efficiency for the same reduction using ZnS with dihydrofuran as the sacrificial donor.

Table 1 shows that over a broad range of oxide catalyzed reactions in water, yields of C_1 products are very small, in the μM range, and similar to our results for formate and acetate. Many of the published reports describe finding methane and methanol but not formate, the initial reduction product. Methane is the one C_1 product that is not susceptible to reoxidation by

aqueous based TiO_2 or related photocatalysts because it has such low water solubility (about 0.145 mmol CH_4/L/0.1 MPa CH_4, Carroll et al., 1998) and such low reactivity toward oxidation by HO radical (Atkinson, 1985). As a result, methane may simply represent a "survivor" product from both aqueous and gas phase reactions, whereas formate and formaldehyde remain in the water phase, in contact with catalysts and susceptible to reoxidation, thus limiting the yields of these products.

Oxidation of formate (or acetate) likely arises from hole oxidation of formate to the radical, followed by a second oxidation step to form CO_2.

$$h_{VB}^{+} + HCO_2 \longrightarrow HCO_2 \bullet \qquad (R5)$$

$$h_{VB}^{+} + HCO_2 \bullet \longrightarrow CO_2 + H^{+} \qquad (R6)$$

$$h_{VB}^{+} + H_2O \longrightarrow \bullet H_2O^{+} \qquad (R7)$$

$$\bullet H_2O^{+} \longrightarrow HO \bullet + H^{+} \qquad (R8)$$

$$HO \bullet + HCO_2^{-} \longrightarrow H_2O + \bullet CO_2^{-} \qquad (R9)$$

$$HO \bullet + HCO_2 \bullet \longrightarrow H_2O + CO_2 \qquad (R10)$$

$$4\ HO \bullet \longrightarrow 2H_2O + O_2 \qquad (R11)$$

Reactions (R7) and (R8) indicate that in the absence or near absence of organic material, hole oxidation of water will produce hydroxyl radical (HO or HO •) or the equivalent TiO • radical (Hoffmann et al., 1995). Competition between HO • and h_{VB}^{+} also may occur with some reducing agents such as formate , wherein H-atom abstraction is favored by HO •, but electron transfer is favored by h_{VB}^{+} (Sun and Pignatello, 1995). With either oxidant, as organic compounds build up in concentration, both oxidants will begin to oxidize them in competition with the kinetically much slower oxidation of water (R5/R6 versus R7). HO radical reacts with organic compounds by H-atom transfer to form water and organic radicals as in R9 (Buxton et al., 1988)). The relative importance of competing reactions R5/R6, R7 and R9 is determined by the relation between the rate of formation of HO and the rate of formation of formate through reduction of CO_2 (R4).

At some point in the photoprocess, competition between reduction of CO_2 and oxidation of formate (or CH_2O or CH_3OH) will lead to a steady state for formate concentration. Experiments in Tables 2 and 3 are not rigorous tests of this idea, but the results suggest that the steady state for formate could lie in the range of 22-45 μM (1-2 ppm), possibly higher for

acetate. Buxton et al (1988) report the relative reactivities of formate and acetate toward HO radical is about 40:1, implying that acetate formation is greatly favored in a competitive HO radical reoxidation process, even if its formation from CO_2 is disfavored by kinetics and photo requirements.

CONCLUSIONS

The micromolar yields found for formation of C_1 products by aqueous photoreduction of CO_2 with oxide semiconductor photocatalysts such as TiO_2 for the most part replicates reports by other investigators. Published reports of significantly larger concentrations of formate and formaldehyde could not be duplicated under what appear to be very similar conditions of light intensity, catalyst and CO_2 concentrations. Experimental artifacts may be involved in some cases, where earlier investigators used the Nash method to measure formate and formaldehyde, possibly leading to artificially high values in the presence of dissolved CO_2. Also, very high yields found in some CO_2 reductions entailed use of sacrificial electron donors such as sulfite, methanol, propanol, and dihydrofuran.

Measured quantum efficiencies for TiO_2 and $SrTiO_3$ photoreductions are on the order of 0.1-0.2% or about 80 times smaller than the efficiency for oxidizing formate back to CO_2 under argon and about 200 times smaller than for oxidizing formate under oxygen. The ratio of the two former efficiencies would place an upper limit on formate formation of 40-50 μM unless some means were found to remove formate (and other products) from the reaction zone. An advanced design concept for continuously removing aqueous phase products from the reactor is one approach to overcome this limitation. Another approach would optimize a vapor phase reduction process with gaseous or supercritical CO_2 and water vapor, which might also drive the reduction to form volatile C_1 products such as methanol and methane.

In several experiments, we used oxide photocatalysts treated to enhance their visible light absorption properties by coating with iron oxide or cyanide complexes. In one case Sb and Cr were incorporated into $SrTiO_3$ to do the same thing. Platinum islands were deposited on TiO_2 to also enhance reduction. Only Pt/TiO_2 showed an enhanced rate of reduction by a factor of about two. Neither of the iron treated catalysts nor the Sb-Cr enhanced catalyst was found to have any activity beyond that found for the parent catalyst. Hematite-coated TiO_2 showed no evidence of any photoreductive capacity, possibly because the hematite absorbs most visible and near UV light without generating any useful concentration of reductive carriers.

A first order assessment of the spatial requirements for solar reduction of CO_2 produced in a large electricity plant gives a minimum of 10 km^2 if the photocollection and photoreduction efficiencies were each 100%. If combined efficiencies were only 10%, the required area would be close to 100 km^2 or 40 mi^2. This 10 km^2 estimate is further idealized in relying on summer

intensities under clear skies at mid latitude. Winter intensities are reduced by a factor of up to three. If catalyst efficiencies could be raised to the range of 10% without use of sacrificial donors and with collection efficiencies of 50%, the spatial requirement would still be large-100 km^2 or 38 mi^2. Whether efficient catalysts can be found and incorporated into an efficient solar collector system remains unknown at this time.

Implicit in the spatial calculations is the assumption that storage capacity is built into the system to reduce the 24-hour production of CO_2. Nonetheless, the diurnal character of sunlight places an additional requirement on the practical design: how to store nightime-produced CO_2 for next-day reduction.

Despite the admittedly limited scope of the present investigation, several recommendations seem appropriate: (1) restrict consideration of the application of solar-driven CO_2 reduction to CO_2 sources of less than 1000 MW/day capacity; (2) intiate research aimed at developing more efficient photocatalysts for CO_2 reduction in classes of photosemiconductors where intrinsic efficiencies for absorption of solar radiation extend to 600 nm to ensure that if high reductive efficiency is achieved, the catalyst also has high solar absorption efficiency as well—one without the other is of little value; (3) extend efforts to reduce CO_2 reduction from the aqueous phase to the gas or supercritical phase to minimize reoxidation of products by physically isolating the products from the reaction zone.

REFERENCES

Atkinson, R. 1985. *Chem. Rev*. **85**:69.

Butler, J. N. 1981. Carbon Dioxide Equlibria, Addison-Wesley, Menlo Park, CA 1981, pp. 5-6.

Bunce, N. J., J. LaMarre, and S. P. Vaish. 1984. *Photochem. Photobiol*. 39:532.

Buxton, G. V., C. L. Greenstock, W. P. Helman, and A. B. Ross. 1988. *J. Phys. Chem. Data* **17**:513-886.

Calvert, J. G. and J. V. Pitts, Jr. 1966. Photochemistry, John Wiley and Sons, New York, pp. 783-786.

Carroll, J. J., F-Y Jou, A. E. Mather, and F. D. Otto. 1998. *Can. J. Chem. Engr.* **76**:945.

Cornu C., A. J. Colussi, and M. R. Hoffman. 2001. *J. Phys. Chem. B* **105**:1351.

DoE (2001), Proceed. Conference on CO_2 Sequestration, Washington, DC, May 14-16.

Eggins, B. R., P.K.J. Robertson, E. P, Murphy, E. Woods, and J.T.S. Irvine. 1998. *J. Photochem. Photobiol. A Chem.* **118**:31.

Geoastro. 1999. www.geoastro.de/daylight.

Goren, Z., A. J. Nelson, and A. J. Frank. 1990. *J. Phys. Chem.* **94**:3784.

Halmann, M. M. and M. Steinberg. 1999. Greenhouse Gas Carbon Dioxide Mitigation, Lewis Publishers, Boca Raton, FL.

Henglein, A. 1984. *Pure Applied Chem.* **56**:1215.

Hirano, K., E. Suzuki, A. Ishikawa, T. Moroi, H. Shiroishi, and M. Kaneko. 2000. *J. Photochem. Photobiol. A Chem.* **136**:157.

Hoffmann, M. R., S. C. Martin, W. Choi, and D. W. Bahnemann. 1995. *Chem Rev*. **95**: 69.

Ikeue, K., S. Nozaki, M. Ogawa, and M. Anpo. 2002. *Catal. Lett.* **80**:111.

Inoue, H., T. Tarimeto, T. Sakata, H. Mori, and H. Yoneyama. 1990. *Chem. Lett.* 1483.

Irvine, J.T.S., B. R. Eggins, and J. Grimshaw. 1990. *Solar Energy* **45**:27.

Ishikawa, A., T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen. 2002. *J. Am. Chem. Soc.* **124**:13547.

Ishitani, O., C. Inoue, Y. Suzuki, and T. Ibusuki. 1993. *J. Photochem. Photobiol. A Chem.* **72**:269.

Jain, S., J. Vardia, A. Sharma, and S. C. Ameta. 2001. *Int. J. Energy Res.* **25**:107.

Kato, H. and A. Kudo. 2002. *J. Phys. Chem.* B **106**:5029.

Kim, S. and W. Choi. 2002. *J. Phys. Chem.* B **106**:13311.

Kisch, H. and G. Twardzik. 1991. *Chem. Ber.* **124**:1161.

Leifer, A. 1988. The Kinetics of Environmental Photochemistry. ACS Professional Reference Book, Washington, D.C.

Lewis, N. S. 1998. *J. Phys. Chem.* B **102**: 4843.

Licht, S. and H. Tribusch. 2000. *J. Photochem. Photobiol.* B **104**:8920.

Mill, T., W. R. Mabey, D. C. Bomberger, T. W. Chou, and D. G. Hendry. 1982. Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water. U.S. EPA, Washintton, D.C., EPA 600/3-82-002.

Mill, T. 2002. Unpublished results.

Miyasaka, T., T. Watanabe, A. Fujishima, and K. Honda. 1979. *Nature* **277**:637.

Mizuno, T., K. Adachi, K. Ohta, and A. Saji. 1996. *J. Photochem. Photobiol. A Chem.* **98**: 87.

Nash, R. 1953. *Biochem. J.* **55**:416.

Ohta, K., Y. Ueda, S. Nakaguchi, and T. Mizuno. 1998. *Can. J. Chem.* **76**:228.

Penpolcharoen, M., R. Amal, and V. Chen. 1998. Proc 25th Australasian Chem.Eng. Conf. – CHEMECA '98, p. 222.

Revkin, A. 2000. Warming effects to be widespread, New York Times, June 12.

Sayama, K. and H. Arakawa. 1993. *J. Phys. Chem.* **97**:531.

Sharma, B. K., R. Ameta, J. Kaur, and J. C. Ameta. 1997. *Int. J. Energy Res.* **21**:923.

Stevens, W. K. 2000. Seas and soils emerge as keys to climate, New York Times, May 16.

Sun, Y. and J Pignatello 1995. *Environ. Sci. Technol.* **29**: 2065.

Taka, T. and K. Domen. 1998. *Catal. Today* **44**:17.

Ulman, M., B. Aurian-Bajeni, and M. Halmann. 1982a. *Isr. J. Chem.* **22**:177.

Ulman, M., A.H.A. Tinnemans, A. Mackor, B. Aurian-Blajeni, and M. Halmann. 1982b. *Int. J. Solar Energy* **1**: 213.

Upadhya, S. and D.F. Ollis. 1997. *J. Phys. Chem B* **101**: 2625.

Yao, C.C.D., M. Su, and T. Mill. 1995. Preprint Extend. Abstract, Div. Environ. Chem., Amer Chem. Soc. Meet, Chicago, IL, August 20-24.

Yoneyama, H. 1997. *Catal. Today* **39**:169.

Zepp, R. and Cline. 1977. *Environ. Sci. Technol.* **11**:359.

Zou, Z. and H. Arakawa. 2001. *Nature* **414**:625.